PROCESS FOR THE PREPARATION OF STABILIZERS FOR POLYMERS

The instant invention relates to a process for the preparation of stabilizers for polymers, especially for polyamides.

The service life of polyamides is dependent on the raw materials used within the manufacturing process, the additives used in stabilizing the polymer against damage brought about by melt-processing and environmental weathering factors. A serious drawback to providing stabilization systems for polyamides lies in the fact that maximum concentration of many additives is limited. Polyamides are regarded as poor in solvating additives, especially non-polar additives having relatively low molecular weight in relation to the polyamide polymer. On the other hand, manufacturers of polyamide-based molded and extruded goods strive to include low concentrations of additives for economic reasons.
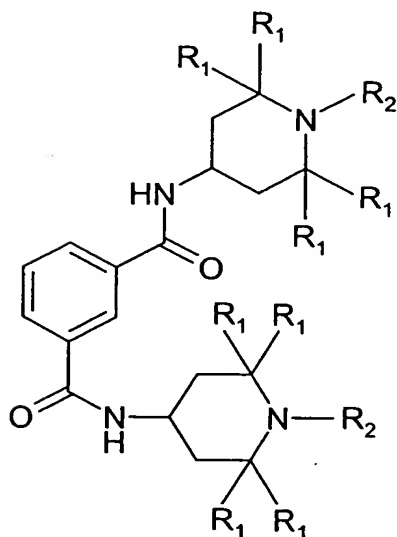
Some of the stabilizers or stabilizer systems which are used for stabilization of polyamide are mentioned for example in US 4,003,875 (unsymmetrical oxalic acid dianilides), US 5,045,083 (copper complexes and oxanilide UV absorbers), US 4,544,691 (oxalanilides, benzalmalonates, α-cyanocinnamates and o-hydroxyphenylbenzotriazoles), US 5,338,319 (copper complex and oxalic acid diaryl amide) or US 5,380,774 (hindered phenolic antioxidant, phosphite, hindered amine stabilizer and optionally a benzotriazole).

Polyamide polymers are characterized by high tensile strength, abrasion resistance, however polyamides require also stabilization against thermo-oxidative and photodegradation to sustain these properties in their long-term applications.

Polyamides must accept lightfast dying systems in addition. Discoloration of the matrix is regarded to be highly critical and may cause shade changes in colored articles, e.g. fibres and moldings of polyamide polymers.

Therefore further improvement in the stabilization systems of polyamide polymers is always needed.

The most powerful stabilizer generally used for the stabilization of polyamides first mentioned in WO 97/43335 can be seen in general formula (I) (definition of radicals see below)
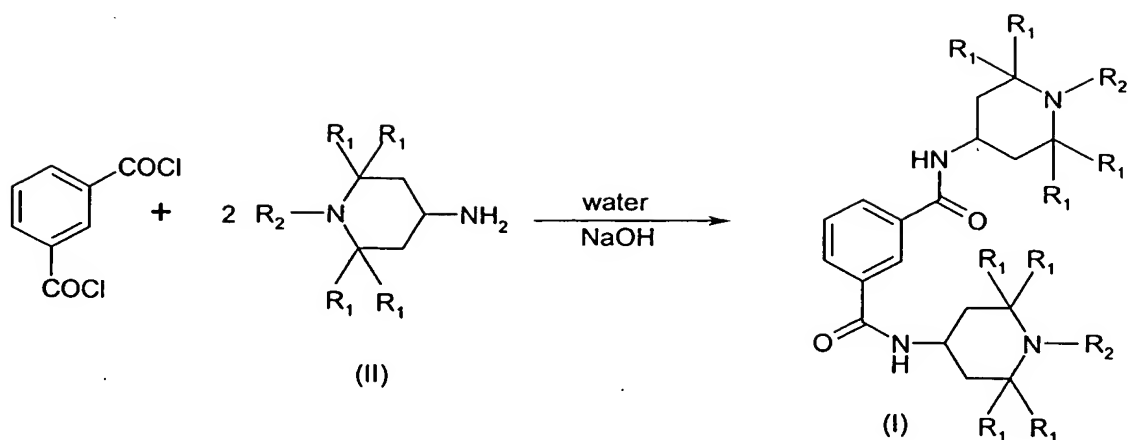

(I)

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This powerful stabilizer can be added in the melt of polyamides and improves heat stability, light stability, chemical stability and dye affinity of the polyamide polymer.

10   In the meantime new stabilizer systems were found which combine the unique properties of (I) in synergistic combinations together with other additives. Examples therefore can be found in EP 0903372 A1 or US 6,063,843. Compound (I) or derivatives thereof can also successfully be used for the stabilization of polyester resins as can be seen in EP 1000967 A1.

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Originally, stabilizers of general formula (I) were synthesized by condensation of isophthalic acic dichloride (IPC) with sterically hindered amines of general formula (II), where radicals R_1 and R_2 are defined below. Water was used as a solvent for this reaction.

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(II)   (I)

For achieving acceptable yields, excess of the amine component (II) had to be used.

5   Amine components of general formula (II) are generally known to be poorly biodegradable.

As the excess of the amine component had to be washed out after reaction with water, waste water was produced which cannot be treated effectively in conventional sewage

10   plants.

The yields which could be achieved by the above mentioned process were limited, due to hydrolysis with water which occurred during reaction phase.

15   Thus this process known from the prior art could not be transferred to a regular production plant, due to the mentioned disadvantages.
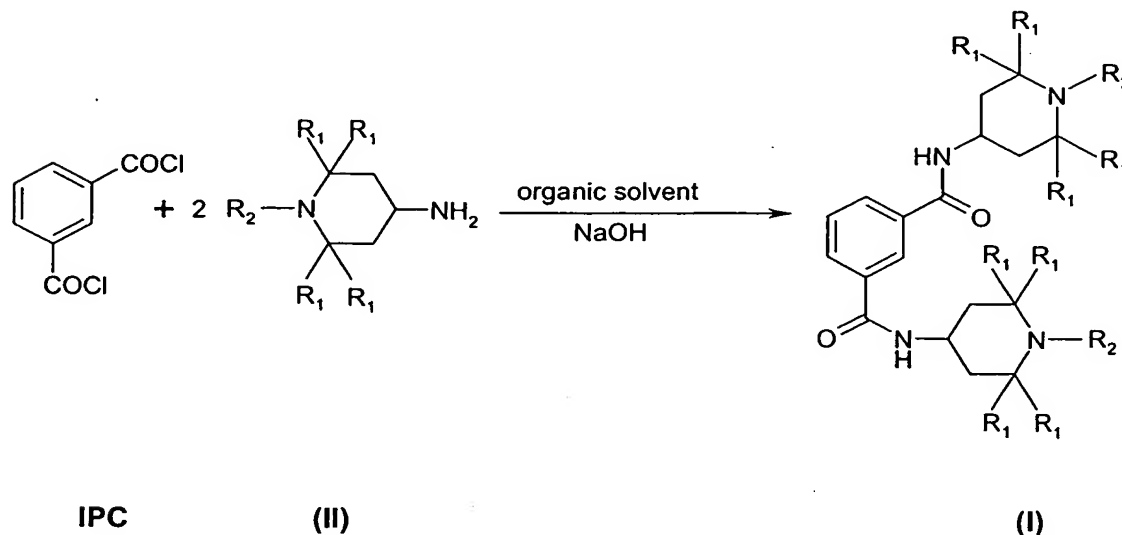
GENERAL DESCRIPTION OF THE INVENTION

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It has now been found that the use of certain organic solvents together with an optimized combination of pressure and temperature leads to a surprising increase of the overall yield of more than 10 % and to less environmental problems by a reduced organic load of the waste water.

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Therefore object of the instant invention is a process for the preparation of stabilizers of general formula (I) by condensation of isophthalic acic dichloride (IPC) with sterically hindered amines of general formula (II),

IPC   (II)   (I)

wherein R_1 is H, C_6-cycloalkyl or C_1-C_4-alkyl, and R_2 is H, C_1-C_5-alkyl, or a C_1-C_{10}-alkyloxy-group, characterized in that organic solvents or mixtures thereof with water and an optimized combination of pressure and temperature are used during the whole process.

Preferably R_1 is H or C_1-C_2-alkyl and R_2 is H or C_1-C_2-alkyl, most preferably R_1 is methyl and R_2 is H.

The reaction between IPC and component (II) is carried out by stirring IPC into a solution containing compound (II), 30-70 %, preferably 40-60 %, most preferably 50 % by weight of aqueous caustic soda, organic solvent and water.

One key step of the invention is the use of organic solvents or mixtures of organic solvents with water instead of water alone as in the prior art. The solvents used are organic aromatic hydrocarbons, preferably xylene, or aliphatic alcohols, preferably ethanole or isopropanole. Most preferably isopropanole or mixtures of isopropanole with water are used.

The preferred ratio of isopropanole to water is from 60-80 % isopropanole to 20-40 % water, most preferably the ratio is 70 % isopropanole and 30 % water by volume.

By using mentioned solvents or mixtures of these solvents with water, the yield could be improved from 85 % to 96 % of theory; that means that hydrolysis-reaction could be minimized.

5   Also the excess of the bio-toxical amine component (II) could be avoided without reducing yield. The instant process uses a molar ratio of IPC and the amine component (II) of 1 mole IPC to 1.80-2.00 mole of (II), preferably 1.80-1.90 mole of (II), most preferably a molar ratio of 1 mole IPC to 1.85 mole of (II) is applied. This leads to a minimum organic load of waste water, which has significant advantages in respect to

10 the mentioned biotoxical properties of component (II).

However the instant solvent system alone cannot eliminate completely the problems of the process of the prior art. Even by using mixtures of water and an organic solvent at ambient pressure, (I) is isolated as small, sticky, cake-like particles, which cannot be

15 isolated easily on conventional filtration aggregates like centrifuges or suction filters. As consequence big amounts of water had to be applied in order to wash effectively and to reach acceptable product quality.

Therefore a further key of this invention is the instant combination of reaction

20 conditions like temperature and pressure. Thereby as a further advantage filtration properties of the crystals of the compound of general formula (I) could be improved significantly.

Addition of IPC to the amine (II) in the solvent/water/NaOH solution is performed at

25 temperatures from 20-40°C, preferably 25-35°C, most preferably at 30°C.

After addition of IPC has completed, the reaction mixture is stirred for 50 to 70 minutes, preferably for one hour at the same temperature. The reaction mixture is then heated in an autoclave to 90 - 110 °C, preferably to 100°C and to a system pressure of 1.3 to 1.7

30 bars, preferably of 1.5 bars. Under these conditions the reaction product is completely dissolved in the solvent and 2 phases can easily be separated.

The aqueous layer which contains most of the salts, excess of caustic and some residues of isopropanole, can be easily separated and – after redistillation of the

35 residual solvent – be further treated in a conventional sewage plant.

After addition of water, the organic layer is heated to a temperature of 130-140°C and a system pressure of 3.0-4.0 bars until all of the solid has dissolved. The reaction mixture now is cooled to ambient temperature and large crystals of products of general formula (I) are formed, which can be isolated by using conventional filter aggregates.

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By using the instant process, the yield of the reaction could be raised to 96 %, waste water consumption and load could be reduced significantly and the filtration properties of the reaction product formed could be optimized, which leads to maximum output of products of formula (I) in a regular production plant. The instant process therefore is

10   ecologically advantageous.

The instant process leads to stabilizers of general formula (I), which can also be used in stabilizer systems as indicated in US 6,063,843. Also further additives can be added according to different applications. These further additives are also described in US

15   6,063,843.

EXAMPLES

The given examples shall illustrate the advantage of the novel process for preparation of stabilizers of general formula (I). Examples are used, where radicals R_1 = methyl, and R_2 = H. The stabilizer of formula (I) with R_1 = methyl, and R_2 = H is generally well-

5   known as a powerful stabilizer for polyamide polymers and commercialized by Clariant under the brand name Nylostab® S-EED®.

EXAMPLE 1

10   In a 4-necked 2 l flask with stirrer, dropping funnel, thermometer and pH electrode

    150.5 g   of 2,2,6,6-Tetramethylpiperidin-4-yl-amine (98.7 %; 0.95 mole) and

    85.2 g   of 50% NaOH solution (1.07 mole) are added to a mixture of

    470.0 g   of isopropanol and

    260.0 g   of demin. water.

15   Under stirring

    102.1 g   of molten isophthalic acid chloride (99.4 %; 0.50 mole) are added.

The temperature of the reaction mixture is held at 30°C during dosage of IPC by cooling with an ice bath. The reaction mixture is stirred for another 1 hour under the

20   same conditions (temperature / pH-control). A white suspension is being formed during this reaction phase. The reaction mixture is transferred to a 3 l laboratory autoclave with stirrer and internal thermometer and the mixture is heated to a temperature of TI = 100°C. The resulting pressure of the system is about 1.5 bar and the solid is being dissolved completely.

25   Two liquid phases are being formed:

    -    Lower aqueous phase containing salts and aqueous NaOH and some isopropanole

    -    Upper organic phase containing desired product solved in isopropanole;

30   The lower phase is removed under pressure and

    950.0 g   of demin. water is added to the reaction mixture.

The mixture is further heated up to TI = 130° C and a corresponding system pressure of about PI = 3.3 bar until all of the solid has completely dissolved. The suspension is

35   allowed to cool down to ambient temperature TI ≈ 30°C. The resulting white suspension is passed through a filter aggregate with metal screen and the reaction

product is washed with 715.0 g of demin. water to remove chloride and other impurities. The reaction product is heated in a vacuum drying oven until constancy of weight. The yield of reaction product of general formula (I) with R_1 = methyl, and R_2 = H is 200.0 g or 95.3 % of theoretical value (yield based on minor component TAD).

EXAMPLE 2 (Comparison Example):

In a 4-necked 2 l flask with stirrer, dropping funnel, thermometer and pH electrode

161.2 g	of 2,2,6,6-Tetramethylpiperidin-4-yl-amine (98.7 %; 1.02 mole) and
93.8 g	crushed ice

are cooled to a temperature of 7°C.

Under stirring

| 102.1 g | of molten isophthalic acid chloride (99.4 %; 0.50 mole) are added. |

The temperature of the reaction mixture is held below 10°C during dosage of IPC. After addition of IPC the sticky mass is diluted with

450.0 g	of demin. water and
133.3 g	of 30 % NaOH (1.00 mole) is added.

During addition of NaOH

| 300.0 g | of demin. water is added to dilute the reaction mass. |

After 3 h of stirring at 25°C the sticky suspension is filtered on a laboratory suction filter and washed until the pH reaches a value of 10 (in total 2400 g of demin. water are needed).

The filter cake again is suspended in

| 600.0 g | of demin. water, stirred for 30 min and again is isolated on a laboratory suction filter and washed with 700.0 g of demin. water. |

The reaction product is heated in a vacuum drying oven until constancy of weight. The yield of reaction product of general formula (I) with R_1 = methyl, and R_2 = H is 184.8 g or 83.6 % based on IPC.

TABLE 1

Main Results of Examples 1 (Novel Process) and Comparison Example 2 (Old Process):

	Example 1	Example 2
Amount (TAD*) g/batch	150.5	161.2
Yield of (I) g; %	200.0; 95.3	184.8; 83.6
Filtrate 1 amount (g)	524.0	438.6
COD** mg/l	12000	45000
TAD filtrate 1 (g)	none	0.5
Waste Water 1 amount (g)	328.5	2363
COD** mg/l	5200	5000
TAD in waste water 1 (g)	none	0.03
Filtrate 2 amount (g)	none	690
COD** mg/l	none	1900
TAD filtrate 2 (g)	none	0.002
Waste Water 2 amount (g)	none	2800
COD** mg/l	none	1300
TAD in waste water 2 (g)	none	none

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*   TAD: 2,2,6,6-Tetramethylpiperidin-4-yl-amine

**   COD: Chemical oxygen demand: oxygen equ. needed for oxidation of organic load in waste water

10   As can be seen in table 1, the amount of TAD/batch needed for reaction in example 1 is significantly lower than in example 2. Nevertheless, the isolated yield of reaction product of formula (I) is about 12 % higher than in example 2.

The amount of waste water needed as well as the amount of residual TAD in waste

15   water is much lower in comparison to example 2 as can be seen in table 1.
   Therefore the novel inventive process not only means a progress in respect to the advantageous reaction conditions in example 1, but also in respect to the waste water consumption and load being produced.

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EXAMPLE 3

The filtration properties of crystals of the reaction product (I) with radicals R_1 = methyl, and R_2 = H of examples 1 and 2 were tested on a standard filtration unit. This unit consists of a steel pressure filter (I = 0.5 m; d = 0.05 m; Co. BHS; metal screen porosity 60 μm). The filter unit is filled with a standard volume (800 ml) of the product suspension of (I). The filter unit is closed and a pressure of 1 bar N_2 is applied. The filtration time is measured as a function of the volumes of filtrate being produced during filtration. A good filtration time correlates with good filtration properties of the suspension:

TABLE 2

Filtration properties of the product suspension of (I) on a standard BHS filter-unit

Filtrate	time (s)			
	100 ml	200 ml	300 ml	400 ml
example 1	3	11	22	35
example 2	40	175	370	470

As can be seen in table 2, the filtration properties of the suspension of example 1 are much better compared to the filtration properties of suspension in example 2. As this results correlate with the filtration properties on a regular production filter aggregate, a much higher capacity can be achieved by using the new production process.